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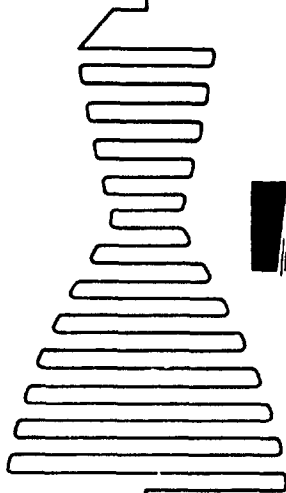
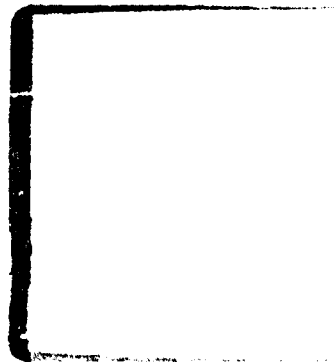
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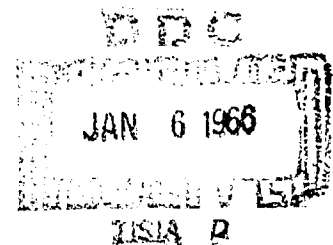


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6633 CANOGA AVENUE, CANOGA PARK, CALIFORNIA

R-5883-5

(Unclassified Title)

QUARTERLY PROGRESS REPORT,  
INORGANIC HALOGEN OXIDIZERS

(29 August 1965 through 28 November 1965)

Group 4  
Downgraded at 3-Year Intervals  
Declassified After 12 Years

Contract Nonr 4428(00)

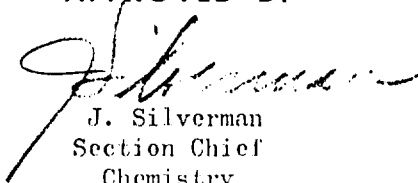
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FOREWORD

The research reported herein was supported by the Advanced Research Projects Agency through the Office of Naval Research, Power Branch, Code 429, with Mr. Richard L. Hanson as Scientific Officer. This report was prepared in compliance with Section H of Contract Nonr 4428(00) under ARPA Order No. 23, and covers the period 29 August 1965 through 28 November 1965. This work was carried out in the Synthetic Chemistry Group with Dr. D. Pilipovich, Principal Scientist. Full-time associates connected with the technical effort were Dr. H. F. Bauer, responsible for coordinating this report; Dr. C. J. Schack; and Dr. C. B. Lindahl.

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### ABSTRACT

The fluorination of KF and CsF complexes of  $\text{Cl}_2\text{O}$  has yielded  $\text{ClF}_3\text{O}$ . Thermal dissociation of  $\text{KClF}_4\text{O}$  occurred below ambient temperature while heating was required to dissociate  $\text{CsClF}_4\text{O}$ .

Oxychlorine trifluoride has also been prepared from chlorine nitrate in a 95+ percent yield by fluorination of the complex  $\text{CsClFONO}_2$ . The reaction was independent of the presence of  $\text{N}_2\text{O}_4$ . Glow discharge experiments at  $-196^\circ\text{C}$  with solid  $\text{Cl}_2\text{O}$  and activated fluorine gas have resulted in small quantities of  $\text{ClF}_3\text{O}$ , but  $\text{ClF}_5$  and  $\text{FClO}_2$  were the major products.

The hydrolysis of  $\text{ClF}_5$  with potassium fluoride dihydrate and excess potassium fluoride was carried out in a flow system. No  $\text{ClF}_3\text{O}$  was obtained.

The ratio of CsF to  $\text{ClF}_3\text{O}$  in this complex has been determined to be 1.15 when using excess  $\text{ClF}_3\text{O}$ . Experiments with excess CsF also demonstrated an incomplete attainment of stoichiometry indicating unfavorable kinetics for the reaction. Reversible dissociation of the complex occurs below  $150^\circ\text{C}$ .

The basic behavior of  $\text{ClF}_3\text{O}$  was shown by its reaction with  $\text{PF}_5$  and  $\text{SiF}_4$  to form 1:1 and 2:1 complexes respectively. The reaction of  $\text{ClF}_3\text{O}$  with  $\text{FNO}$  to form a reversible

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complex demonstrated its acidic properties. Oxychlorine trifluoride was displaced from its  $\text{CsF}$  complex by  $\text{ClF}_3$  and from its  $\text{PF}_5$  complex with  $\text{FNO}$ . Vapor pressure/temperature equations for the  $\text{ClF}_3 \cdot \text{FNO}$  and  $(\text{ClF}_3)_2 \cdot \text{SiF}_4$  complexes were obtained.

The synthesis of  $\text{ClF}_5\text{O}$  was attempted by the fluorination of  $\text{CsClF}_4\text{O}$  and by the reaction of  $\text{KrF}_2$  with  $\text{ClF}_3\text{O}$ . Oxychlorine trifluoride was recovered in each case. Partial fluorination of  $\text{Cl}_2\text{O} \cdot \text{CsF}$  was investigated as a route to chlorosyl fluoride and gave only traces of an unidentified substance thought to be  $\text{FClO}$ . The reduction of  $\text{ClF}_3\text{O}$  as a possible route to  $\text{FClO}$  was tried with the reducing agents  $\text{Cl}_2\text{O}$ ,  $\text{SO}_2$ ,  $\text{Br}_2$ , and  $\text{BrF}_3$ .

The complex of  $\text{Br}_2\text{O}$  and  $\text{CsF}$  has been fluorinated in hopes of forming  $\text{BrF}_3\text{O}$  or  $\text{BrF}_5\text{O}$ .

The fluorination of  $\text{N}_2\text{O}$  in the presence of  $\text{CsF}$  was attempted as a possible path to new F, N, O compounds. Neither complex formation nor reaction with fluorine was noted.

In an effort to demonstrate the existence of mercury hypochlorite as a possible intermediate, reaction products of  $\text{Cl}_2$  and  $\text{HgO}$ , as well as  $\text{Cl}_2\text{O}$  and  $\text{HgCl}_2$ , were studied. No direct or reproducible evidence supporting mercury hypochlorite structures was obtained.

(Confidential Abstract)

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#### INTRODUCTION

During the present quarter, the studies revolving around oxychlorine trifluoride were expanded. In addition to studying the chemistry of its formation and intermediates involved, some attention was given to the chemistry of  $\text{ClF}_3\text{O}$  itself.

The chemistry of  $\text{ClF}_3\text{O}$  thus far is being pursued in two ways. The most important is the potential of  $\text{ClF}_3\text{O}$  as an intermediate in both fluorinations and reductions. Accordingly, the results of Rocketdyne studies in this connection will be presented in detail. Acid-base equilibria involving  $\text{ClF}_3\text{O}$  are also of interest. Some new species derived from  $\text{ClF}_3\text{O}$  in this context have been partially characterized.

Because preliminary characterization of  $\text{ClF}_3\text{O}$  is complete, more attention has been devoted to seeking other oxyhalogen fluorides. In this vein, fluorination studies of  $\text{Br}_2\text{O}$  were resumed.

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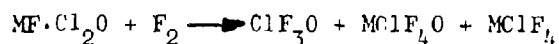
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## TECHNICAL DISCUSSION

## FLOROX STUDIES\*

Synthesis of Oxychlorine Trifluoride From  
Cl<sub>2</sub>O-Alkali Metal Fluoride Complexes

The fluorination of Cl<sub>2</sub>O, complexed with alkali metal fluorides, has continued to provide the primary route to ClF<sub>3</sub>O:



When CsF was used, part of the ClF<sub>3</sub>O was evolved by warming to room temperature. Additional ClF<sub>3</sub>O as well as ClF<sub>3</sub> was obtained by thermal dissociation of the residual solids.

In contrast, no additional ClF<sub>3</sub>O was evolved when the products from the fluorination of KF·Cl<sub>2</sub>O were heated above ambient temperature. The total yield was obtained by simply warming to ambient temperature. When the other product, ClF<sub>3</sub>, was driven off by heating, the potassium fluoride could be reused with no loss of efficiency, similar to the satisfactory reuse of CsF in these fluorination reactions.

The ease of workup from KF-containing fluorinations suggests that KClF<sub>4</sub>O is appreciably dissociated at ambient temperature while CsClF<sub>4</sub>O requires considerable heating for complete dissociation. Moreover, a simple technique for the separation of ClF<sub>3</sub> from ClF<sub>3</sub>O may be possible using KF. It was found that CsF was unsuitable in this regard.

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\*Unclassified designation for ClF<sub>3</sub>O

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While a high conversion of  $\text{Cl}_2\text{O}$  to  $\text{ClF}_3\text{O}$  was not achieved using potassium fluoride, reasonably good yields have been obtained during initial experiments. At first, a yield of 9 percent based on  $\text{Cl}_2\text{O}$  was achieved. Subsequent runs in the same container gave yields of 44 percent based on  $\text{Cl}_2\text{O}$  and, following KF regeneration, 43 percent based on KF in a run with excess  $\text{Cl}_2\text{O}$ .

#### Electric Discharge Fluorination of Solid $\text{Cl}_2\text{O}$

Earlier in this program, the use of electric-discharge-activated fluorine was tried in reactions with solid  $\text{Cl}_2\text{O}$  to achieve the synthesis of  $\text{ClF}_3\text{O}$ . At that time (Ref. 1), it was observed that some  $\text{ClF}_5$  was found but no  $\text{ClF}_3\text{O}$ . This reaction was re-examined using recirculated fluorine in a closed-loop system at low pressures rather than the simple flow-through method. As expected, a much more efficient fluorination was achieved. The yield of  $\text{ClF}_5$  was approximately 45 percent (based on  $2\text{ClF}_5$  for each  $\text{Cl}_2\text{O}$ ). In addition, small quantities of  $\text{ClF}_3\text{O}$  were found along with some  $\text{ClF}_3$  and much  $\text{FClO}_2$ .

Therefore, with the incorporation of this improved technique, the general utility of the electric discharge fluorination process has been improved and made more efficient. Also, it is expected that this activated gas-solid reaction method might now be employed to demonstrate the synthesis of other highly fluorinated species, in particular  $\text{ClF}_5\text{O}$ .



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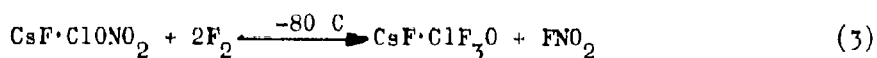
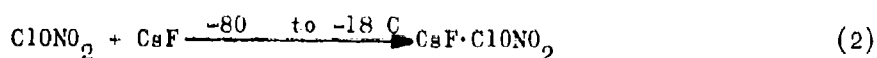
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### Synthesis of Oxychlorine Trifluoride from $\text{ClONO}_2$

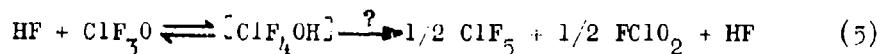
Two additional syntheses of  $\text{ClF}_3\text{O}$  via  $\text{ClNO}_3$ ,  $\text{CsF}$ , and  $\text{F}_2$  have been conducted in the same manner as reported previously (Ref. 2). The first, employing previously used  $\text{CsF}$ , gave no product. The second, utilizing fresh  $\text{CsF}$ , gave a 95+ percent yield of  $\text{ClF}_3\text{O}$ . In this reaction, it was noted that some of the  $\text{ClF}_3\text{O}$  was obtained as part of the volatile species, whereas in the past, it was observed only on pyrolysis of the solids left after completion of the fluorination. Nitryl fluoride was the only other major product obtained, thus confirming the postulated reaction sequence:



It is also noteworthy that the  $\text{ClNO}_3$  employed in this high-yield  $\text{ClF}_3\text{O}$  synthesis was contaminated with  $\text{NO}_2$ . The  $\text{NO}_2$  impurity had no detrimental effect other than to consume fluorine in being converted to  $\text{FNO}_2$ .

### Hydrolysis of $\text{ClF}_5$ With Potassium Fluoride Hydrate

Previous attempts (Ref. 3) to produce  $\text{ClF}_3\text{O}$  by hydrolysis of  $\text{ClF}_5$  have unsuccessfully utilized metal fluoride hydrates. Because  $\text{HF}$  is a product of such a reaction it may have been detrimental to the formation of  $\text{ClF}_3\text{O}$ :



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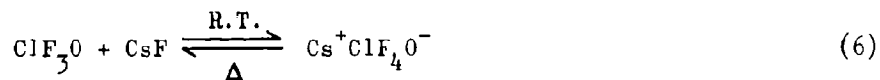
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Therefore, the reaction was repeated using  $\text{ClF}_5$ ,  $\text{KF} \cdot 2\text{H}_2\text{O}$ , and a large excess of  $\text{KF}$  so that the  $\text{HF}$  formed would be tied up as  $\text{KHF}_2$ . Chlorine pentafluoride at 60-mm pressure was passed through a 10:1 powdered mixture of  $\text{KF}$  and  $\text{KF} \cdot 2\text{H}_2\text{O}$  in a Kel-F flow reactor. The first reaction yielded  $\text{FClO}_3$ ,  $\text{FClO}_2$ ,  $\text{Cl}_2$ , and noncondensibles. The second reaction gave mostly  $\text{FClO}_2$  and small amounts of  $\text{FClO}_3$ .

The third reaction gave  $\text{FClO}_2$  and unreacted  $\text{ClF}_5$ . The reactivity of  $\text{ClF}_3\text{O}$ , if formed, is apparently greater with metal fluoride hydrates than is  $\text{ClF}_5$ .

#### Studies of the Cesium Oxychlorine Tetrafluoride Complex

The reversible nature of the  $\text{CsF}-\text{ClF}_3\text{O}$  system has been reported (Ref. 2).



However, no information regarding the actual stoichiometry was obtained because all the earlier experiments were conducted with a large molar excess of  $\text{CsF}$ . When the complex formation was carried out using measured amounts of  $\text{CsF}$  and  $\text{ClF}_3\text{O}$ , and with an excess of the latter, an experimental composition  $\text{CsF}_{1.15} \cdot \text{ClF}_3\text{O}$  was obtained. This composition is reasonably close to a 1:1 complex, especially considering the problem of solid/liquid contact.

The formation of cesium oxychlorine tetrafluoride was also examined using excess  $\text{CsF}$  rather than excess  $\text{ClF}_3\text{O}$ . After 3 days at ambient temperature, 83 percent of the  $\text{ClF}_3\text{O}$  was complexed and after 3 weeks at  $-16^\circ\text{C}$ , 96  $\pm$  3 percent of the  $\text{ClF}_3\text{O}$  was complexed. The failure of all the  $\text{ClF}_3\text{O}$  to be

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complexed is attributed to poor gas/solid contact after all the liquid  $\text{ClF}_3\text{O}$  has reacted because the  $\text{Cs}^+\text{ClF}_4\text{O}^-$  complex has a negligible vapor pressure of  $\text{ClF}_3\text{O}$  even at room temperature.

Because cesium oxychlorine tetrafluoride has potential utility as an intermediate in the synthesis of chlorosyl fluoride or oxychlorine pentafluoride, its thermal stability is of interest. Available data indicate that  $\text{ClF}_3\text{O}$  can be completely liberated from the cesium fluoride complex by pumping for several hours at 130 C. However, the nature of the complex giving rise to  $\text{ClF}_3\text{O}$  in this reaction was not accurately known because it was the result of the fluorination of the  $\text{Cl}_2\text{O} \cdot \text{CsF}$  complex. An attempt was made to thermally dissociate any  $\text{Cs}^+\text{ClF}_4\text{O}^-$  present, leaving the byproduct  $\text{ClF}_3$  in the complex form  $\text{Cs}^+\text{ClF}_4^-$ . The temperature required to liberate  $\text{ClF}_3\text{O}$  completely was well below that required to yield  $\text{ClF}_3$  from  $\text{Cs}^+\text{ClF}_4^-$  (Ref. 4). Yet, evolved  $\text{ClF}_3\text{O}$  was mixed with appreciable amounts of  $\text{ClF}_3$ . This observation might be indicative of the retention of a fluorinated  $\text{ClOCl}$  moiety such as  $\text{Cs}_2\text{ClF}_8\text{O}$ . It is planned to check this possibility by heating a mixture of the independently prepared salts,  $\text{Cs}^+\text{ClF}_4\text{O}^-$  and  $\text{Cs}^+\text{ClF}_4^-$ , to see if the  $\text{ClF}_3\text{O}$  evolved in this case is also mixed with  $\text{ClF}_3$ . If warranted, additional studies with X-ray powder diffraction will be carried out.

#### Reactivity of Oxychlorine Trifluorine With Monel

Previous experiments in Monel with  $\text{F}_2$  showed 63- to 70-percent  $\text{ClF}_3\text{O}$  recovery at 200 to 236 C over 16-hour periods (Ref. 2). It was recently found that heating  $\text{ClF}_3\text{O}$  with  $\text{CsF}$  to 200 C in Monel for 3 days, converted all the  $\text{ClF}_3\text{O}$  to  $\text{FClO}_2$ ,  $\text{ClF}$ , and  $\text{ClF}_3$ . These conflicting results may be the result of the formation of the  $\text{F}_2\text{ClO}$  radical which, in absence of fluorine, reacted with an incompletely passive Monel surface. It may be

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recalled that 16-hour experiments in stainless steel at 200 C gave only  $\text{Cl}_2$  and  $\text{O}_2$  (Ref. 2) in the absence of fluorine. It is possible that while  $\text{F}_2\text{ClO}$  is a hypothetical precursor to  $\text{FClO}_2$ ,  $\text{ClF}_3$ , and  $\text{ClF}$  in Monel, the same radical could give  $\text{Cl}_2$  and  $\text{O}_2$  with the more reactive stainless steel.

#### Oxychlorine Trifluoride Reactions With Acidic and Basic Fluorides

The ability of chlorine trifluoride to form complexes with both alkali metal fluorides and strong Lewis acids has been demonstrated with oxychlorine trifluoride as well. In addition to the previously reported reactions with boron trifluoride and arsenic pentafluoride (Ref. 2),  $\text{ClF}_3\text{O}$  reacted with both phosphorus pentafluoride and silicon tetrafluoride to form solid complexes. Phosphorus pentafluoride formed a colorless 1:1 complex with  $\text{ClF}_3\text{O}$ , which had less than 20 mm Hg pressure at ambient temperature. The solid could be moved by pumping but was presumably dissociated in the gas phase because no infrared spectral differences could be seen between the individual components and the vapor above the complex. A less stable complex was formed when  $\text{ClF}_3\text{O}$  and  $\text{SiF}_4$  were mixed. When equimolar parts were brought to -80 C. one half of the  $\text{SiF}_4$  reacted. Upon the addition of another equivalent portion of  $\text{ClF}_3\text{O}$ , the balance of the  $\text{SiF}_4$  was complexed after temperature cycling. The vapor pressure of the 2:1  $\text{ClF}_3\text{O-SiF}_4$  mixture was measured at several temperatures between -80 and 14 C and the following vapor pressure/temperature equation was obtained:

$$\log_{10} p(\text{mm}) = 7.75 - 1545/T \quad (7)$$

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The enthalpy and entropy changes for the process  $(\text{ClF}_3\text{O})_2 \cdot \text{SiF}_4$  (solid)  $\rightarrow$   $2\text{ClF}_3\text{O}$  (gas) +  $\text{SiF}_4$  (gas) were calculated:  $\Delta \tilde{H} \sim 22$  kcal,  $\Delta \tilde{S} \sim 65$  e.u. An estimation of the enthalpy change in the process  $2\text{ClF}_3\text{O}$  (l) +  $\text{SiF}_4$  (g)  $\rightarrow$   $(\text{ClF}_3\text{O})_2 \cdot \text{SiF}_4$  (s) was made from the heats of vaporization and sublimation of  $\text{ClF}_3\text{O}$  and  $\text{SiF}_4$ :  $\Delta \tilde{H} \sim 2$  kcal. The complex may be written as either  $(\text{ClF}_2\text{O}^+)_2 \text{SiF}_6^-$  or  $\text{ClF}_3\text{O} \rightarrow \text{SiF}_4 \rightarrow \text{OClF}_3$ . Successive portions of the complex were removed at  $-23^\circ\text{C}$ . Their infrared spectra showed a constant ratio of  $\text{ClF}_3\text{O}$  and  $\text{SiF}_4$  absorbances indicating a 1.9 mole ratio.

The amphoteric behavior of  $\text{ClF}_3\text{O}$  was further demonstrated by its acidic reaction with nitrosyl fluoride. Apparently two complexes are formed,  $\text{FNO} \cdot \text{ClF}_3\text{O}$  and  $\text{FNO} \cdot 2\text{ClF}_3\text{O}$ . The former complex was converted to the latter by pumping at  $-80^\circ\text{C}$ . A vapor pressure/temperature curve was obtained for the  $\text{FNO} \cdot \text{ClF}_3\text{O}$  complex from  $-80$  to  $0^\circ\text{C}$ :

$$\log_{10} p(\text{mm}) = 8.47 - 1625/T \quad (2)$$

The heat of reaction for the combination of the liquids  $\text{FNO}$  and  $\text{ClF}_3\text{O}$  to form the solid complex was calculated as about 5 kcal/mole of complex from the heats of vaporization of the liquids and the above equation.

The relatively high density, 1.9 g/cc, and heat of vaporization, 7.7 kcal/mole, of  $\text{ClF}_3\text{O}$  (Ref. 2) may be indicative of the existence of dimeric or bridged species in the liquid, e.g.,  $\overset{\delta+}{\text{ClF}_3\text{O}} - \overset{\delta-}{\text{O}} - \overset{\delta-}{\text{ClF}_3}$ . The addition of fluoride might then result in the formation of the observed 2:1 complex  $\text{NO}^+ \text{ClF}_4^- \text{O} - \overset{\delta-}{\text{O}} - \text{ClF}_3$ .

When an equimolar amount of nitrosyl fluoride was added to the  $\text{ClF}_3\text{O} \cdot \text{PF}_5$  complex at  $-80^\circ\text{C}$ ,  $\text{ClF}_3\text{O}$  was liberated.

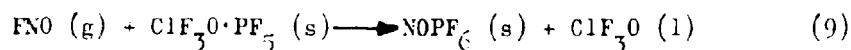
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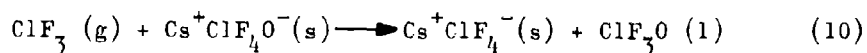
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An infrared spectrum of the products volatile at room temperature showed only  $\text{ClF}_3\text{O}$  indicating the following reaction:



Thus, as expected,  $\text{ClF}_3\text{O}$  is a weaker base to  $\text{PF}_5$  than is  $\text{FNO}$ .

Oxychlorine trifluoride was also displaced from its complex with a fluoride base by using another acid. Addition of  $\text{ClF}_3$  to  $\text{CsClF}_4\text{O}$  at ambient temperature liberated  $\text{ClF}_3\text{O}$  according to the equation:

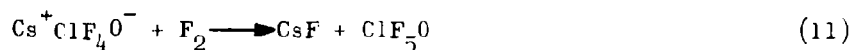


This confirms  $\text{ClF}_3$  to be a stronger Lewis acid than  $\text{ClF}_3\text{O}$  toward  $\text{CsF}$ .

#### STUDIES LEADING TO NEW OXIDIZERS

##### Attempted Synthesis of Oxychlorine Pentafluoride

Oxychlorine trifluoride provides a potential intermediate for making both chlorosyl fluoride and oxychlorine pentafluoride. By analogy with the fluorination of  $\text{Cs}^+\text{ClF}_4^-$  to yield  $\text{ClF}_5$ , the fluorination of the complex  $\text{Cs}^+\text{ClF}_4\text{O}^-$  would be expected to be a likely route to the new oxychlorine fluoride,  $\text{ClF}_5\text{O}$ .



Experiments with increasingly vigorous conditions of temperature and pressure have not resulted in  $\text{ClF}_5\text{O}$  or any other new compounds.

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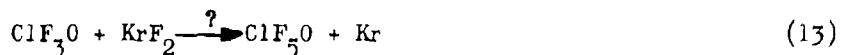
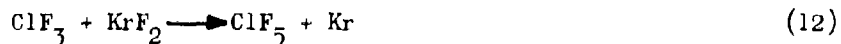
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Conditions imposed thus far have been 750 psi at 50 C, 850 psi at 100 C, and 1200 psi at 160 C. The  $\text{ClF}_3\text{O}$  was recovered essentially unchanged from the Monel reactor in each case.

Another possible route to  $\text{ClF}_5\text{O}$  is the direct fluorination of  $\text{ClF}_3\text{O}$  by  $\text{KrF}_2$  (Ref. 5) at low temperatures. The possible utility of this reaction is indicated by the recent report of the preparation of  $\text{ClF}_3$  and  $\text{KrF}_2$  (Ref. 6).



Good mixing of the reactants can only be achieved at temperatures above -65 C, the melting point of  $\text{ClF}_3\text{O}$ . In three reactions so far conducted, the materials were allowed to warm up together from that temperature to ambient temperature over several hours. No evidence was found, however, for the formation of any new materials. The  $\text{KrF}_2$  underwent smooth thermal decomposition to Kr and  $\text{F}_2$ , and some  $\text{ClF}_3$  contaminant was partially converted to  $\text{ClF}_5$ ; the  $\text{ClF}_3\text{O}$  was recovered quantitatively. Additional experiments are planned using shorter warming periods.

## Reduction of Florox

The nonvolatile solid formed by low-temperature fluorination of the  $\text{Cl}_2\text{O}$ -CsF complex has been heated to yield  $\text{ClF}_3\text{O}$ ,  $\text{ClF}_3$ , and, on three occasions, ClF and traces of an unknown species. The unknown partially passed through a -156 C trap in a vacuum line. The two bands in the rock salt region were observed and are indicated in Fig. 1. Additional

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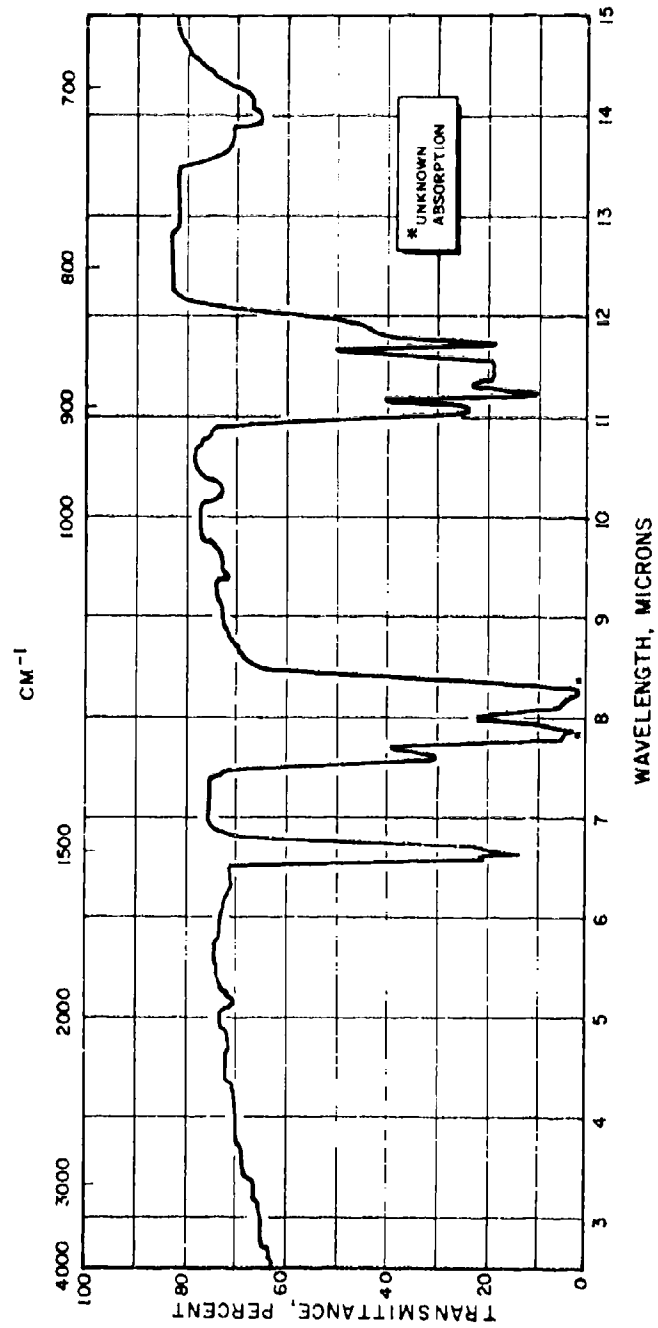


Figure 1. Pyrolysis of Cl<sub>2</sub>O-CsF Fluorination Products

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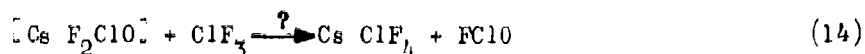
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bands were noted at 645, 650, 610 (a possible pqr), and possibly at 465  $\text{cm}^{-1}$ . This unknown may be a new F, Cl, O compound and specifically may be  $\text{FClO}$ . Mass spectrometric examination of a sample containing the unknown yielded no information. Three attempts to obtain the unknown by methathetical displacement by  $\text{ClF}_3$  were unsuccessful:



Because only traces of the new material were found thus far, several new approaches have been utilized in the search for this elusive material. The concomitant presence (or absence) of  $\text{ClF}$  suggests synthesis of the unknown and  $\text{ClF}$  by a simultaneous degradation of  $\text{Cs}^+\text{ClF}_4\text{O}^-$  and  $\text{Cs}^+\text{ClF}_4^-$  complexes by incomplete fluorination of the  $\text{Cl}_2\text{O}-\text{CsF}$  complex. Routine fluorinations of the  $\text{Cl}_2\text{O}-\text{CsF}$  complex to  $\text{ClF}_3\text{O}$  and  $\text{ClF}_3$  have utilized 3:1  $\text{F}_2:\text{Cl}_2\text{O}$  ratios. Intentional underfluorination to  $\text{FClO}$  and  $\text{ClF}$  would require a  $\text{F}_2:\text{Cl}_2\text{O}$  ratio of 1:1 according to the equation:



The incomplete fluorination at  $-80^\circ\text{C}$  yielded  $\text{ClF}_3\text{O}$  and much unreacted  $\text{Cl}_2\text{O}$  but only traces of the unknown. Apparently once the  $\text{Cl}_2\text{O}-\text{CsF}$  complex was initially attacked by  $\text{F}_2$  it was oxidized all the way to  $\text{ClF}_3\text{O}$  and  $\text{ClF}_3$ .

Another approach to the synthesis of  $\text{FClO}$  involves reaction of  $\text{ClF}_3\text{O}$  with appropriate reducing agents. With the reducing agent  $\text{Cl}_2\text{O}$ ,  $\text{FClO}$  could arise as an oxidation product as well as a reduction product:



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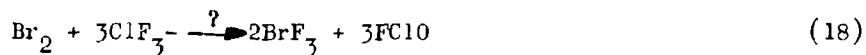
Thus, local excesses would present less of a problem. The experiment was run with equimolar amounts of reactants held at ambient temperature in Monel for 3 days. While all of the  $\text{Cl}_2\text{O}$  reacted, only half of the  $\text{ClF}_3\text{O}$  was used. The products were  $\text{FClO}_2$ , smaller amounts of  $\text{ClF}$ , some chlorine, but no noncondensibles. Either  $\text{FClO}$  did not form or disproportionated according to the equation:



Milder reaction conditions, such as shorter reaction time, lower temperatures, and complexed reactants are indicated for future experiments. Further reaction or disproportionation of any  $\text{FClO}$  formed may be reduced by complex formation as well.

The reaction of sulfur dioxide with  $\text{ClF}_3\text{O}$  was carried out between -80 and 45 C in hopes of fluorinating  $\text{SO}_2$  to  $\text{SO}_2\text{F}_2$  and forming  $\text{FClO}$ . The major reaction products were  $\text{SOF}_2$  and  $\text{FClO}_2$  with minor amounts of  $\text{SO}_2\text{F}_2$ . However, an overall decrease in the pressure of the system of 20 percent suggested some coupling or formation of a less volatile species. Infrared absorptions at 1485, 1240, 880, and  $835\text{ cm}^{-1}$  indicated the presence of  $\text{SF}_4(\text{SO}_3\text{F})_2$  (Ref. 7). Fluorination of this material by  $\text{F}_2$  resulted in  $\text{S}_2\text{O}_6\text{F}_2$  and  $\text{SF}_6$ . No Cl-F absorptions above  $660\text{ cm}^{-1}$  were seen.

The reaction of bromine trifluoride and oxychlorine trifluoride gave no new products. Bromine and oxychlorine trifluoride in a 1:3 mole ratio were reacted by slow warming from -80 C in anticipation of the following result:



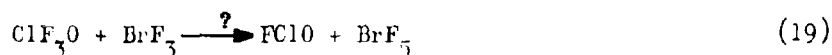
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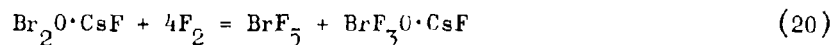
Chlorine, chloryl fluoride, and some unreacted oxychlorine trifluoride were recovered. No evidence for  $\text{BrF}_3$  or  $\text{FClO}$  was obtained. The failure to obtain  $\text{FClO}$  may have been caused by its reaction with bromine. Therefore,  $\text{BrF}_3$  was tried as a reducing reagent:



Bromine trifluoride and oxychlorine trifluoride did not react at room temperature. Higher temperatures may produce the desired reaction.

Attempted Synthesis of Oxybromine  
Fluorides by Fluorination of  $\text{Br}_2\text{O}$

On the basis of analogy with the  $\text{Cl}_2\text{O}$  system, it was expected that  $\text{Br}_2\text{O}$  represents a likely starting material for the preparation of the unknown  $\text{BrF}_3\text{O}$  and  $\text{BrF}_5\text{O}$  compounds. Because of the high melting point of  $\text{Br}_2\text{O}$  and thermal instability above the melting point, the required  $\text{CsF}$  complex was formed using Freon 11 as a solvent for  $\text{Br}_2\text{O}$ . The complex was obtained after removal of the solvent and has been utilized for several fluorination reactions now in progress at  $-50^\circ\text{C}$ . One partially completed experiment has shown that nearly all the added fluorine was consumed. The only volatile products observed, however, were  $\text{Br}_2$  and  $\text{BrF}_5$ . No  $\text{BrF}_3$  would be expected because it forms a stable complex with  $\text{CsF}$ . No new species were noted but this was not particularly discouraging because  $\text{BrF}_3\text{O}$  and possibly  $\text{BrF}_5\text{O}$  could be present as solid  $\text{CsF}$  complexes. Thermal dissociation of these solids is scheduled. The formation of  $\text{BrF}_5$  in good yield was promising and may indicate the following reaction:



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Fluorination of  $N_2O$ 

Success in the CsF-catalyzed low-temperature fluorination of carbon dioxide suggested that the isoelectronic molecule  $N_2O$  might also be fluorinated under similar conditions. The fluorination of  $N_2O$  over dry powdered CsF was carried out in hopes of synthesizing new N, F, O compounds. The vapor pressure of  $N_2O$  over CsF showed no deviation from  $N_2O$  itself over the temperature range over which  $N_2O$  exists as a liquid. The acidity of  $N_2O$  is apparently insufficient to form a CsF complex. Fluorination of the  $N_2O$ -CsF mixture at  $-80^\circ C$  for 5 days resulted in no reaction.

Cesium Fluoride-Chlorine Monoxide Complex Studies

The alkali metal complexes of  $Cl_2O$  and  $Br_2O$  represent a new class of compounds. The stoichiometry and structure of these compounds are of interest not only because of their unique nature but also because they may provide an insight into the paths leading to the formation of oxy-halogen fluorides upon fluorination. An investigation of the cesium fluoride-chlorine monoxide system was undertaken to determine the stoichiometry and stability of complexes. The ratio of  $Cl_2O$  to CsF was found to be variable, decreasing with increased temperature, pumping, and duration of the experiments. Moreover, the ratios were not reproducible. Large excesses of  $Cl_2O$  were held over CsF at  $-80^\circ C$  for 17 days and longer and then pumped overnight to remove uncomplexed  $Cl_2O$ . The resultant ratios were 1.52, 0.82, and 0.25 during three separate experiments under these conditions and point out the nonreproducible surface conditions and degree of contact during formation of  $Cl_2O \cdot CsF$  complexes. The pressure of  $Cl_2O$  above such complexes was less than 4 mm at  $-23^\circ C$ .

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Investigation of Possible Mercury Hypochlorite Formation

In the course of preparing  $\text{Cl}_2\text{O}$  from yellow  $\text{HgO}$  and  $\text{Cl}_2$ , it was observed that at  $-80^\circ\text{C}$  there was some complexing between the generated  $\text{Cl}_2\text{O}$  and the residual mercury salts. To determine if this complexing is caused by  $\text{HgCl}_2$  or hypochlorite formation, several experiments were conducted on the possible reaction of  $\text{HgCl}_2$  and  $\text{Cl}_2\text{O}$  at  $-80^\circ\text{C}$ . The initial experiment indicated that there was some complexing and furthermore that the  $\text{Cl}_2\text{O}$  was converted partially to  $\text{Cl}_2$ . Additional effort and experiments failed to duplicate this first result and showed no complexing or reaction between these materials. Therefore, the observed complexing of  $\text{Cl}_2\text{O}$  in its synthesis from  $\text{HgO}$  remains unexplained.

X-ray powder analysis of the solid product formed by reaction of  $\text{HgO}$  with excess  $\text{Cl}_2$  showed only lines corresponding to  $\text{HgCl}_2$ . Although the possibility of amorphous or isomorphous mercury hypochlorite exists, apparently the only important reaction with excess chlorine is:



The unusual behavior of the solid product (i.e., turning brown and evolution of chlorine) may be attributed to complexes with  $\text{Cl}_2$  or  $\text{Cl}_2\text{O}$ , or amounts of products other than  $\text{HgCl}_2$  too small to be observed by simple X-ray powder analysis.

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## EXPERIMENTAL EFFORT

### PREPARATION OF $\text{Cl}_2\text{O}$

The details of the new static method for preparing  $\text{Cl}_2\text{O}$  have been presented previously (Ref. 2). With the earlier dynamic method it was necessary to use freshly prepared yellow  $\text{HgO}$ . During this period, however, it was determined that the static method is efficient enough to permit the use of commercial yellow  $\text{HgO}$ . While the yields of  $\text{Cl}_2\text{O}$  are not quite as high as those achieved with the fresh  $\text{HgO}$ , they are nevertheless quite good; i.e., 90- to 97-percent  $\text{Cl}_2\text{O}$  using either 1:1 or 2:1  $\text{HgO}$  to  $\text{Cl}_2$  mole ratios. This compares to 95+ percent with fresh  $\text{HgO}$ . Using the flow technique, the commercial material produces only a 20- to 25-percent conversion of the  $\text{Cl}_2$  to  $\text{Cl}_2\text{O}$ . Therefore, if desired, the preparation of fresh  $\text{HgO}$  may be avoided with only minimal loss of efficiency in the conversion using the static technique.

### PREPARATION OF $\text{KrF}_2$

Krypton difluoride was prepared by circulating an approximately 1:1 molar mixture of  $\text{Kr}$  and  $\text{F}_2$  through an electric discharge reactor cooled to  $-196^\circ\text{C}$ . The apparatus and technique are nearly the same as that reported in the literature (Ref. 5). Changing the temperature of the discharge tube to  $-80^\circ\text{C}$  resulted in no reaction.

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11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY	
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13 ABSTRACT The fluorination of KF and CsF complexes of Cl <sub>2</sub> O has yielded ClF <sub>3</sub> O. Thermal dissociation of KClF <sub>4</sub> O occurred below ambient temperature while heating was required to dissociate CsClF <sub>4</sub> O. Oxychlorine trifluoride has also been prepared from chlorine nitrate in a 95+ percent yield by fluorination of the complex CsClFONO <sub>2</sub> . The reaction was independent of the presence of N <sub>2</sub> O <sub>4</sub> . Glow discharge experiments at -196 C with solid Cl <sub>2</sub> O and activated fluorine gas have resulted in small quantities of ClF <sub>3</sub> O, but ClF <sub>5</sub> and FClO <sub>2</sub> were the major products. The hydrolysis of ClF <sub>5</sub> with potassium fluoride dihydrate and excess potassium fluoride was carried out in a flow system. No ClF <sub>3</sub> O was obtained. The ratio of CsF to ClF <sub>3</sub> O in this complex has been determined to be 1.15 when using excess ClF <sub>3</sub> O. Experiments with excess CsF also demonstrated an incomplete attainment of stoichiometry, indicating unfavorable kinetics for the reaction. Reversible dissociation of the complex occurs below 150 C. Oxychlorine trifluoride was displaced from its CsF complex by ClF <sub>3</sub> and from its PF <sub>5</sub> complex with I <sub>2</sub> O. Vapor pressure/temperature equations for the ClF <sub>3</sub> O·FNO and (ClF <sub>3</sub> O) <sub>2</sub> SiF <sub>4</sub> complexes were obtained. The synthesis of ClF <sub>5</sub> O was attempted by the fluorination of CsClF <sub>4</sub> O and by the reaction of KrF <sub>2</sub> with ClF <sub>3</sub> O. Partial fluorination of Cl <sub>2</sub> O·CsF was investigated as a route to chlorosyl fluoride and gave only traces of an unidentified substance thought to be FClO. The reduction of ClF <sub>3</sub> O as a possible route to FClO was tried with the reducing agents Cl <sub>2</sub> O, SO <sub>2</sub> , Br <sub>2</sub> , and BrF <sub>3</sub> . The complex of Br <sub>2</sub> O and CsF has been fluorinated in hopes of forming BrF <sub>3</sub> O or BrF <sub>5</sub> O. (C)		

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KEY WORDS	LINK A		LINK B		LINK C	
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